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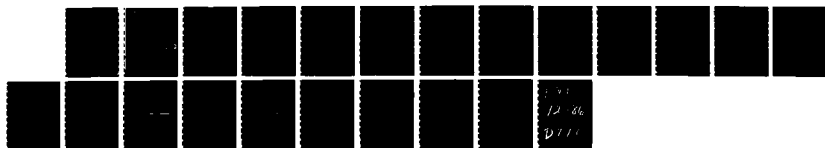
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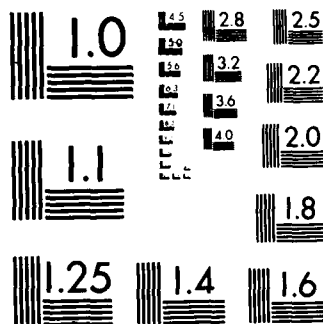
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THERMAL POLYMERIZATION OF ISOMERIC DODECADIENDIYNDIOLS

by

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C Triple bond INTRODUCTION

Recently, the polymerization of acetylenic compounds having two or more acetylene units, $R-(C\equiv C)_n-R'$, has attracted much attention and numerous reports have been published. In the case of diacetylenes, $n=2$, the majority of studies are concerned with the unique topochemical polymerization in crystalline states.¹ However, little has been studied on the thermal behavior of these polyacetylenic compounds, except for diphenyl diacetylenes, although it is known that many of them simply undergo polymerization on heating. When n is greater than four and $R=H$, the compounds become unstable and in many

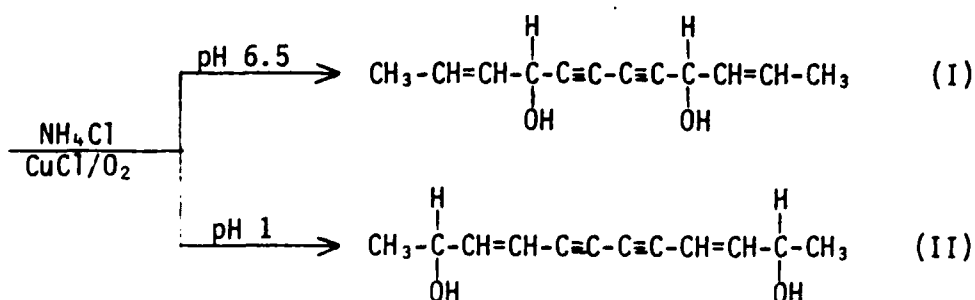
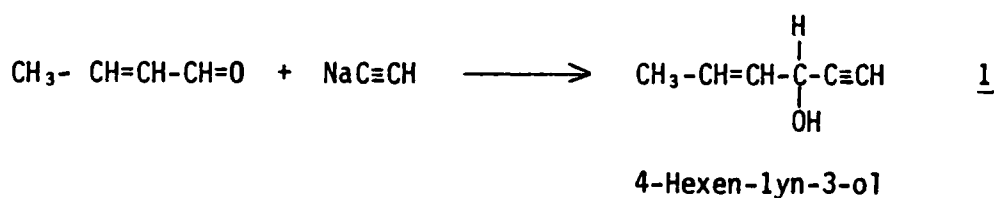
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cases it is difficult to prevent their polymerization on standing. Jones and his coworkers have synthesized many polyacetylenic compounds⁽²⁾ including those occurring naturally in plants of Compositae family. These polyacetylenes contain four or five conjugated acetylenic units linked to the terminal vinyl groups and are reported to be dangerously unstable. Nakagawa³ has prepared diphenyltetraacetylene, which is stable in the dark. Korshak et al.⁴ have claimed that a polyyne with a structure $\text{H}-(\text{C}\equiv\text{C})_n-\text{H}$, and stable up to 2300°C was obtained by the oxidative dehydropolycondensation of acetylene. Although the relationships between stability and structure are not yet clear, all of these compounds are interesting as potential heat resisting materials with high carbon contents.

RESULTS AND DISCUSSION

We prepared 2,10-dodecadien-5,7-diyn-4,9 diol (I) and 3,9-dodecadien-5,7-diyn-2,11-diol (II), which have two acetylene units and two olefinic groups, by the method reported by Jones et al.⁶ as shown below, and their thermal reactions were studied in this work.



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Jones et al. obtained the (I) in 90 percent yield when the coupling reaction was carried out at pH 6.5, whereas (II) was obtained in high yield at pH 1. They reported that (I) rearranges to (II) in the presence of acid, and the melting points of (I) and (II) were cited as 125⁰ and 95⁰ respectively. In this work, the same isomers were obtained as described above. Differential scanning calorimetry of (I) and (II) showed melting temperatures of 124.5⁰ and 93.5⁰C respectively (Figure 1), whereas the broad exotherm at 160-240⁰C may be due to beginning of decomposition.

Characterization of both (I) and (II) was done by ¹H and ¹³C NMR and IR spectroscopy techniques. Figure 2 shows proton NMR spectra of (I) and (II). Olefinic protons α to C \equiv C in (II) gave a doublet at 5.67 ppm ($J=16.9$ Hz), whereas β protons gave doublet of doublet centered at 6.23 ppm ($J=15.75$ Hz), and a multiplet was observed at 4.19 ppm assignable to -CH(OH). Both in (I) and (II), the methyl groups resonate as doublet ($J=6.25$ Hz), but the peak position in (I) was shifted considerably appearing at 1.71 ppm compared to 1.11 ppm for the corresponding resonance in (II). Such a shift may be explained through the olefinic group next to the methyl group in (I). Hydroxyl groups showed as broad peak, and peak area integration was perfect as expected from the structures of (I) and (II).

The C-13 NMR of (I) and (II) are presented in Figures 3 and 4 respectively. The C-13 chemical shifts for 1 and (I) are consistent with those previously observed^{7,8} allowing for solvent-solute effects and instrument variability. For comparison, the chemical shifts for 1 are also included (see Experimental section). Procedures which are common⁹ in C-13 such as off-resonance decoupling multiplicity pattern, chemical shift, data from model compounds, etc.

were used for the resonance assignment. These procedures readily permit the various types of carbons to be distinguished. A comparison between C-13 NMR spectra of (I) and its monoenynol precursor, 4-hexen-1yn-3ol 1, revealed that the chemical shift pattern evident for (I) is very reminiscent of that observed for 1, for example, the methyl and carbinol carbon resonances are very similar. This close analogy also applies to chemical shifts of olefinic carbons, but the acetylenic carbons in (I) are shifted by ca.4 ppm compared with the corresponding carbon in 1.⁸

The simple six-line spectrum observed for symmetrical (I) and (II), derived from six non-equivalent types of carbon atoms, can be divided into three major regions, depending on the hybridization of the carbon. The assignment of SP hybridized carbons of triple bonds was easily made. When two triple bonds are conjugated, as in (I) and (II), the mutual shielding effect of each triple bond resulted in the adjacent α -sp hybridized carbons moving upfield. In (I), the exterior sp hybridized carbons are ca.6 ppm downfield of the interior SP hybridized carbons, while for the (II) the relative difference in shifts is ca.12 ppm. The greater difference between the interior and exterior acetylenic carbons in (II) is presumably due to substituent effects. SP³ hybridized methyl and carbinol carbons for both (I) and (II) were observed in the expected range of chemical shifts, and peaks showed the expected multiplicity. SP² hybridized olefinic carbons in (I) appeared as doublets at 128.99 and 126.09 ppm as it should for any simple olefin, whereas (II) being conjugated alkenyne, the triple bond shields the α -olefinic carbon by ca.23 ppm but deshields the β -olefinic carbon by ca.17 ppm relative to the corresponding alkene.¹⁰ Therefore, olefinic carbons of (II) appeared as doublets distinctly separated at

150.77 and 105.35 ppm. Thus, the chemical shifts and multiplicity of all carbons in (I) and (II) are consistent with the structure described.

The IR spectrum of (I) (Figure 5) showed O-H stretch ($> 3250\text{ cm}^{-1}$), C-O stretch of secondary alcohol with di- α -unsaturation (994 cm^{-1}) together with olefinic C-H stretch (3050 cm^{-1}), and a weak band due to disubstituted unconjugated trans C=C stretch (1672 cm^{-1}). Similar absorptions were seen for (II), including a weak band at 1633 cm^{-1} assigned to the C=C stretching vibration of internal symmetrical disubstituted olefin. Vibrations due to C=C stretch in the range of $2260\text{--}2190\text{ cm}^{-1}$ were almost absent, due to the symmetrical nature of (I) and (II).

Table I shows the conditions of polymerization of (I) and (II) and the characteristics of polymers derived. The results of elemental analysis indicate that there was no appreciable difference in the composition before and after polymerization at 130° or 150°C . Apparently, no decomposition and/or dehydration occurred during the polymerizations conducted at lower temperatures. The polymers obtained at or below 150°C were reddish-brown and those obtained at 500°C were shiny black. Yields of methanol insoluble polymers ranged from 52-79 percent, depending on polymerization conditions and monomer. Typical IR spectrum of polymer (Figure 5) showed broad bands with increased intensity of the absorptions due to conjugated C=C stretching vibrations as compared to that of (I) or (II), suggesting that polymerization proceeds via diacetylenic units, thereby increasing the conjugation in resulting polymer. At the initial stage of polymerization, the polymer was still soluble in dimethylformamide and brittle threads could be drawn from its

molten state, but the longer periods of polymerization gave insoluble and infusible polymers, probably due to increased molecular weight and/or crosslinking. The gel permeation chromatograph of soluble polymers gave a molecular weight of about 1700-2000.

The mass-spectral fragmentation of (I) and (II) at 230°C (Figure 6) produced $M - 15$ (loss of methyl) as initial fragmentation and hydroxyethyl part of (II) corresponding to ca.40 percent weight loss observed in TGA of (II) as shown in Figure 7. Under same conditions, (I) lost little less than 25 percent of its weight up to 200°C due to random scission across olefinic linkage beside the methyl group loss, as evidenced by corresponding fragmentation peaks in mass spectrum of (I). Neither (I) nor (II) decomposed appreciably below 150°C as shown in Figure 7 and Table I, but lost their weight continuously with increase in temperature, (I) losing its total weight at 800°C. On the other hand, polymers I-500-2 and II-500-2 showed no weight loss below 500°C (Figure 8) and polymer II-500-2 retained ca.50 percent of its weight at 1000°C, while polymer I-500-2 lost its weight completely. These results are not surprising because of an extended enyne conjugation in (II) yielding more conjugated polymer II-500-2 and subsequently more graphitization. Conductivity measurements support these findings. The electrical conductivity of polymer II-500-2 was found to be $3.6 \times 10^{-2} \Omega^{-1}$, while polymer I-500-2 showed conductivity of $5 \times 10^{-6} \Omega^{-1}$ under the same conditions. Polymerization of (I) and (II) at 400°C for four hr in a sealed tube gave dark-brown polymers with conductivity of the order of $10^{-9} \Omega^{-1}$, indicating that no graphitization took place at 400°C. The nature of conductivity was of electronic character, since the measurements with direct and an alternate currents gave same results.

Thus, these studies suggest that highly heat-resistant organic materials could be obtained from conjugated acetylenic compounds, preferably having no aliphatic substituents which decompose at lower temperatures.

EXPERIMENTAL

1 2 3 4 5 6

Synthesis of 4-hexen-1yn-3-ol: $\text{HC}\equiv\text{C}-\text{CH}(\text{OH})-\text{CH}=\text{CH}-\text{CH}_3$: 1

The title compound was prepared from crotonaldehyde and acetylene following the procedure reported by Brandsma.¹¹ Colorless liquid, bp. 49-50°C/10 mm (Lit. 60°C/12 mm) was obtained in 69 percent yields.

NMR: ^1H (δ in ppm): 5.9-5.0 (m, 2H), 4.5 (s, 1H), 3.27 (bs, 1H), 2.26 (d, 1H), 1.4 (d, 3H).

^{13}C : (δ in ppm): 129.46 (d, $J_{\text{CH}} = 146$ Hz, C_4), 128.28 (d, $J_{\text{CH}} = 162$ Hz, C_5), 83.11 (s, C_2), 73.58 (s, C_1), 61.79 (d, $J_{\text{CH}} = 149$ Hz, C_3), 16.98 (q, $J_{\text{CH}} = 126$ Hz, C_6)

where s = singlet, d = doublet, dd = doublet of doublet, q = quartet, bs = broad singlet, m = multiplet.

1 2 3 4 5 6

Synthesis of dodeca-2,10-dien-5,7-diyn-4,9-diol (I): $\text{H}_3\text{C}-\text{CH}=\text{CH}-\text{CH}(\text{OH})-\text{C}\equiv\text{C}-$)₂

1 2 3 4 5 6

and dodeca-3,9-dien-5,7-diyn-2,11-diol (II): $(\text{H}_3\text{C}-\text{CH}(\text{OH})-\text{CH}=\text{CH}-\text{C}\equiv\text{C}-)$ ₂ was performed as reported by Jones and coworkers.⁶ Each product was recrystallized from benzene to give sharp melting crystalline (I), mp. 124.5-125°C and (II) mp. 93.5-95°C.

(I): Elem. Anal. Calcd. for: $\text{C}_{12}\text{H}_{14}\text{O}_2$: C, 75.79; H, 7.37%.

Found: C, 75.76; H, 7.41%.

NMR: ^1H (δ in ppm): 5.80 (m, 1H), 5.53 (m, 2H), 4.79 (bs, 1H), 1.71 (d, $J = 6.5$ Hz, 3H).

^{13}C : (δ in ppm): 128.99 (d, $J_{\text{CH}} = 175$ Hz, C_3), 126.09 (d, $J_{\text{CH}} = 176$ Hz, C_2), 79.02 (s, C_5), 67.33 (s, C_6), 60.55 (d, $J_{\text{CH}} = 146$ Hz, C_4), 16.04 (q, $J_{\text{CH}} = 127$ Hz, C_1).

(II): Elem. Anal. Calcd. for: $\text{C}_{12}\text{H}_{14}\text{O}_2$: C, 75.79; H, 7.37%.

Found: C, 75.78; H, 7.36%.

NMR: ^1H (δ in ppm): 6.23 (dd, $J = 15.75$ Hz, 1H), 5.67 (d, $J = 16.9$ Hz, 1H), 4.64 (bs, 1H), 1.11 (d, $J = 6.5$ Hz, 3H).

^{13}C : (δ in ppm): 150.77 (d, $J_{\text{CH}} = 158$ Hz, C_3), 105.35 (d, $J_{\text{CH}} = 164$ Hz, C_4), 78.70 (s, C_5), 72.87 (s, C_6), 65.49 (d, $J_{\text{CH}} = 146$ Hz, C_2), 21.89 (q, $J_{\text{CH}} = 127$ Hz, C_1).

Polymerization

The polymerizations performed at 130° and 150°C were carried out under inert atmosphere in a tube immersed in an oil bath for fixed intervals of time. Polymers were isolated by pouring contents in methanol. When no methanol insoluble polymer was obtained, the contents were dissolved in acetone and precipitated in hexane. Polymers were purified by reprecipitation method. Heating at 400° and 500°C was made in a Pyrex sealed tube under vacuum. After polymerization, the dark-colored products were ground to powder and washed with methanol to get dark-brown or black shiny materials.

Analytical Procedures

Differential scanning calorimetry was performed on a Perkin-Elmer DSC 1B at a heating rate of $20^\circ\text{C}/\text{min}$ under steady flow of nitrogen. The IR spectra were recorded on a Perkin-Elmer 983 IR spectrometer as KBr pellets. Proton and C-13 NMR spectra were recorded on a Varian EM-360 60 MHz ^1H

spectrometer and Bruker WM 250 FT spectrometer with a carbon-13 frequency of 62.9 MHz respectively, for ten percent solutions in a mixture of CDCl_3 - d_6 DMSO with TMS as an internal standard. Mass spectra were taken on a Hewlett-Packard Model -5985 mass spectrometer with GC/MS system. Samples were heated at 150-230°C, keeping temperature of the ionization chamber at 230°C and ionization potential of 70 eV.

The molecular weights of soluble polymers were determined by gel permeation chromatography (GPC) with DuPont Zoebax PSM-300S, PSM-60S and IBM 10 μm pore size columns in dimethylformamide at flow rate of 1 ml/min, using Water Associate differential refractometer R403 as detector and standard polystyrene calibrated curve. Thermogravimetric analysis (TGA) was performed on DuPont thermo-balance Model 951 at a heating rate of 10°C/min under nitrogen atmosphere. For the conductivity measurements, polymer samples were ground to fine powders and compressed in a teflon ring between tungsten metal rods to get 0.5 mm thick disk of five mm diameter. Resistance of this sample was measured using a Keithley Model 614 Electrometer at 26°C.

ACKNOWLEDGMENT

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TABLE I
Polymerization of (I) and (II) and Polymer Characteristics

Monomer	Polymerization Conditions				Elemental Analysis % (Found)		
	at (°C)	for (hr)	yield ^a %	code	C	H	O
I	--	--	--	--	75.76	7.41	16.28
II	--	--	--	--	75.78	7.36	16.84
I	130	20	--	I-130-20	76.28	6.81	17.05
I	150	2	69	I-150-2	73.51	6.60	--
I	150	40	76	I-150-40	76.01	6.91	16.80
I	500	2	54.2	I-500-2	91.65	3.33	4.29
II	130	20	32 ^b	II-130-20	73.72	7.04	--
II	150	2	43 ^b	II-150-2	75.78	6.67	16.47
II	150	30	79	II-150-30	73.97	6.49	18.60
II	500	2	52	II-500-2	90.40	3.25	4.48

a. Methanol insoluble polymer.

b. No methanol insoluble polymer was obtained. Yield represents polymer obtained by precipitation in hexane from acetone solution.

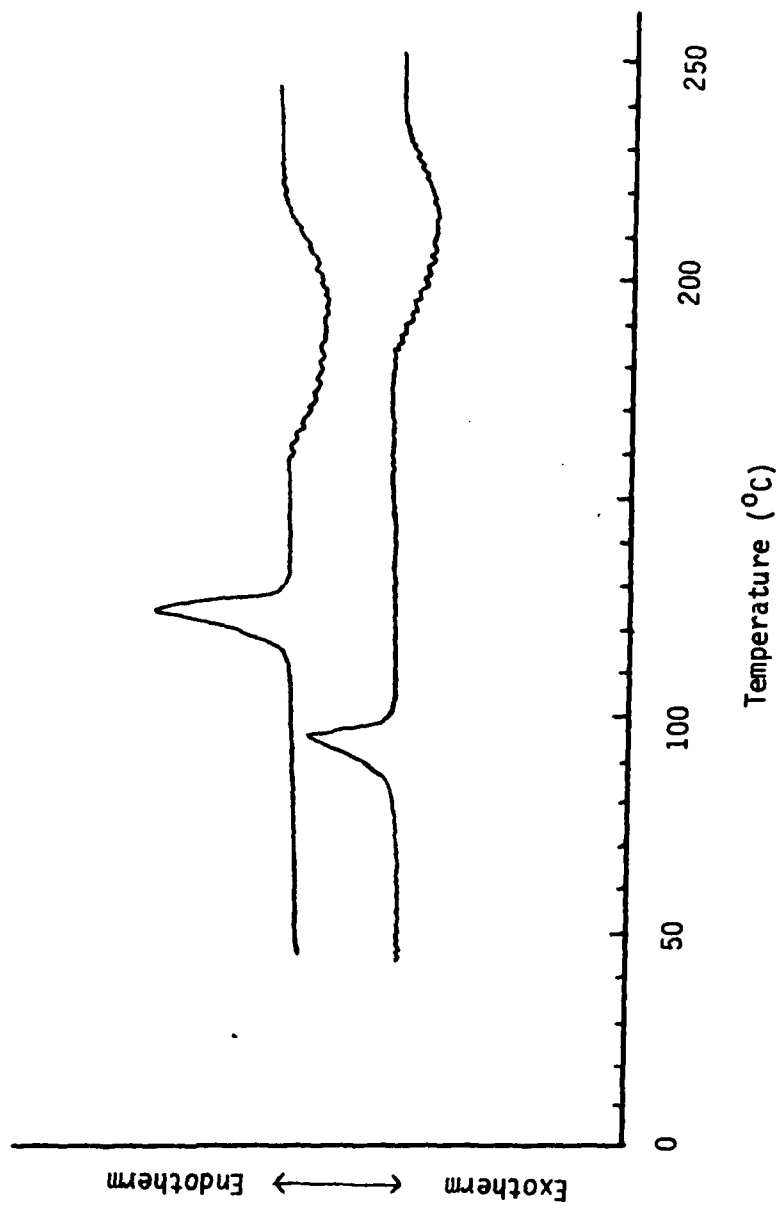


FIGURE 1

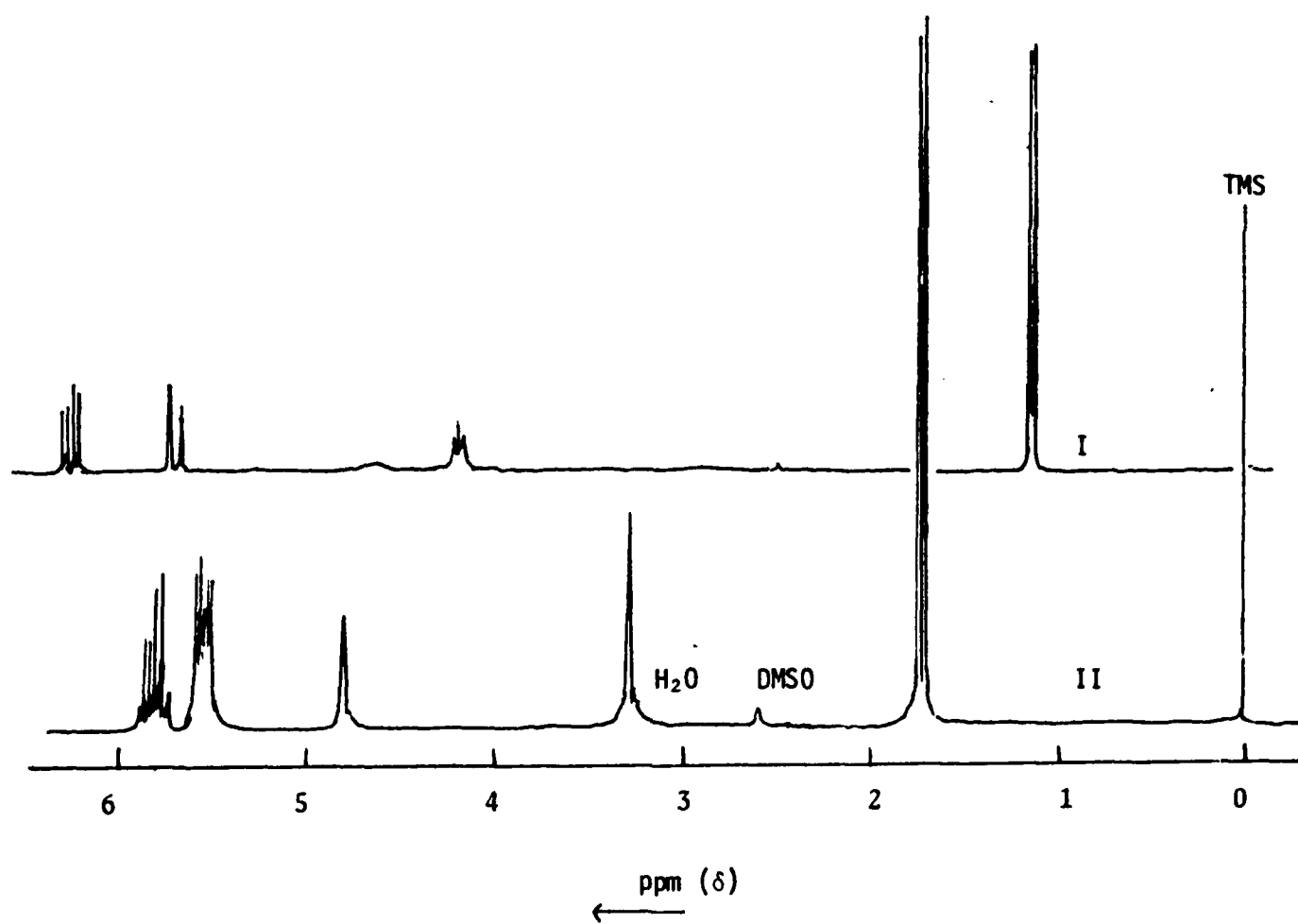


FIGURE 2

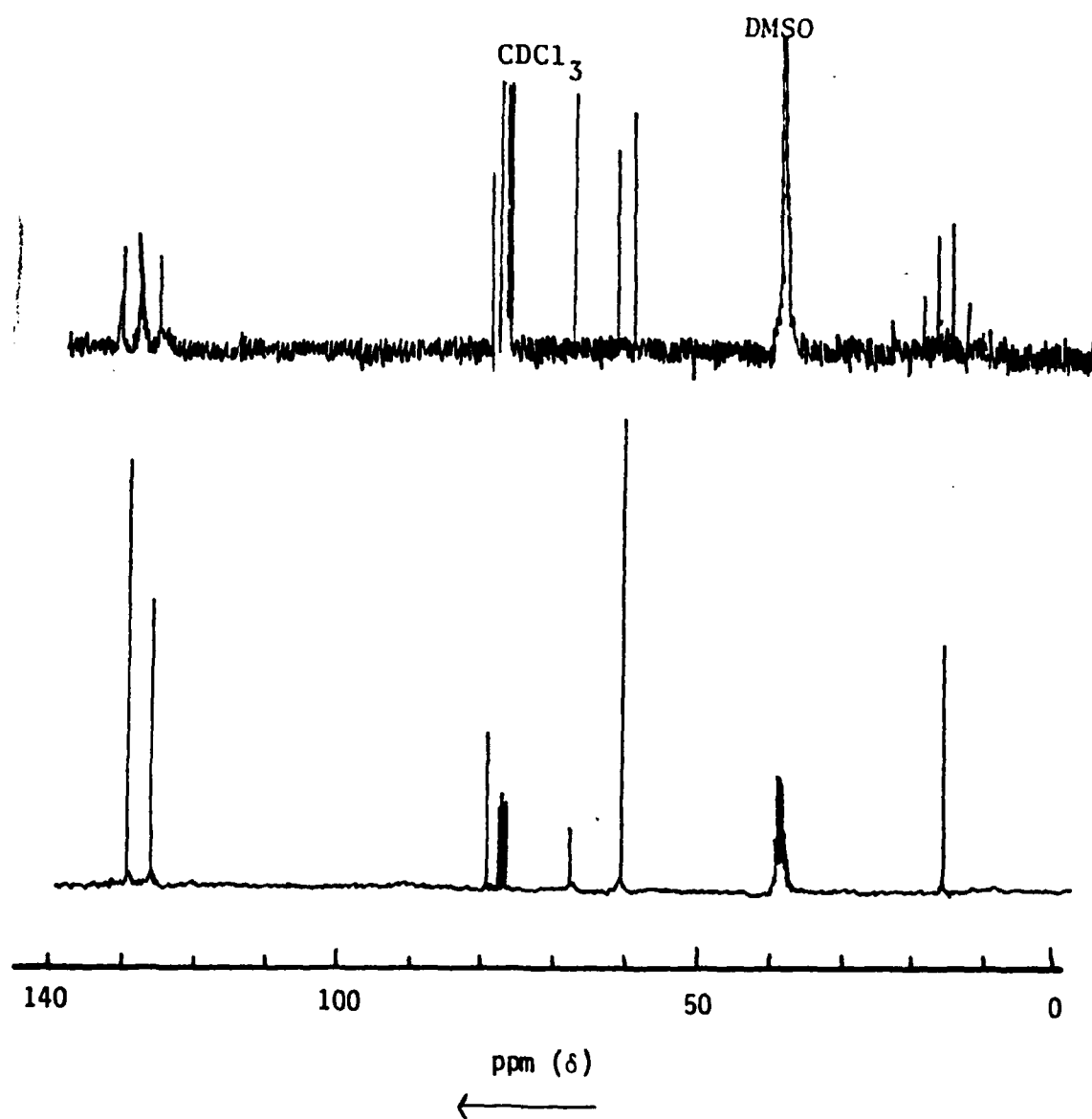


FIGURE 3

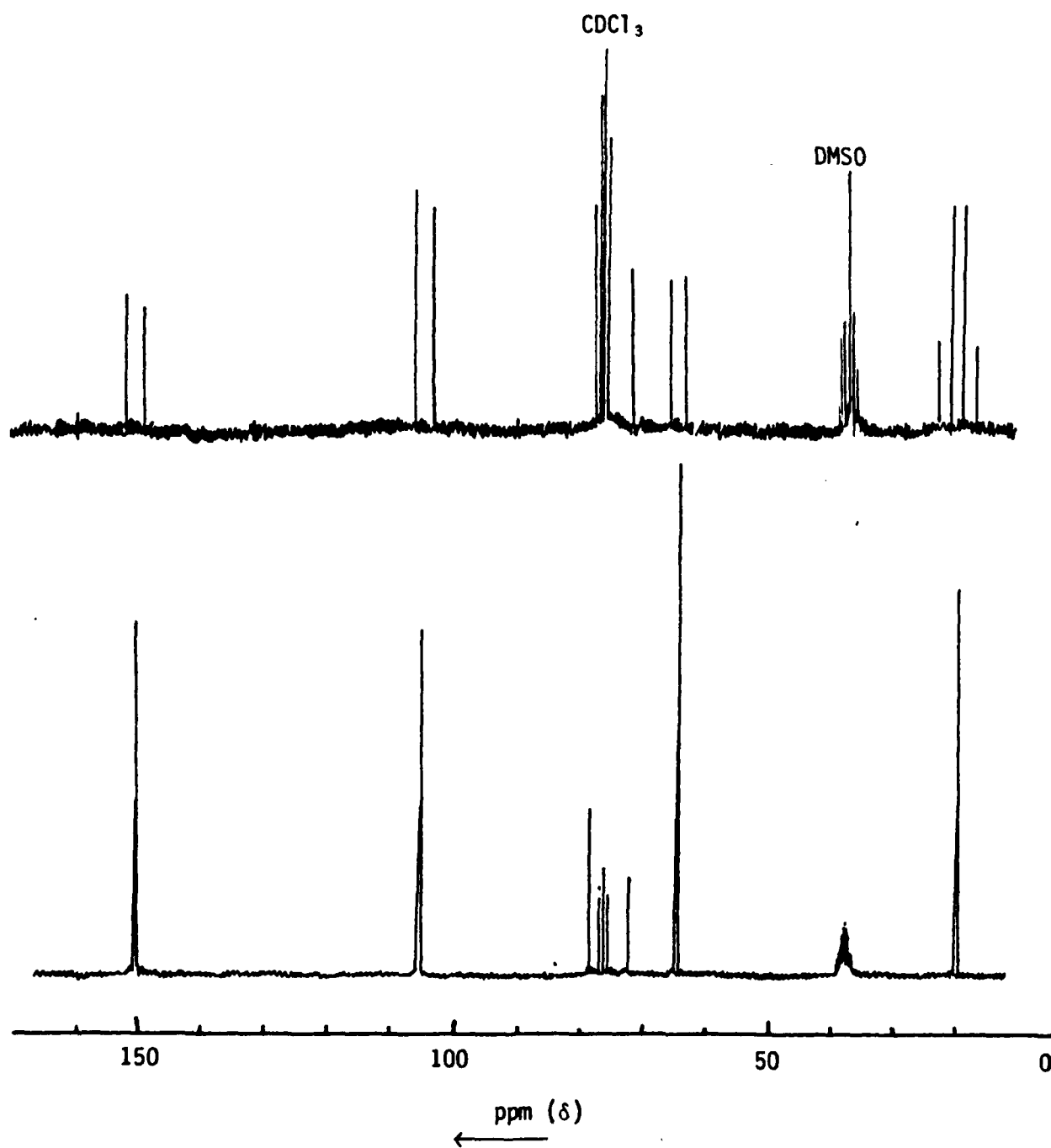


FIGURE 4

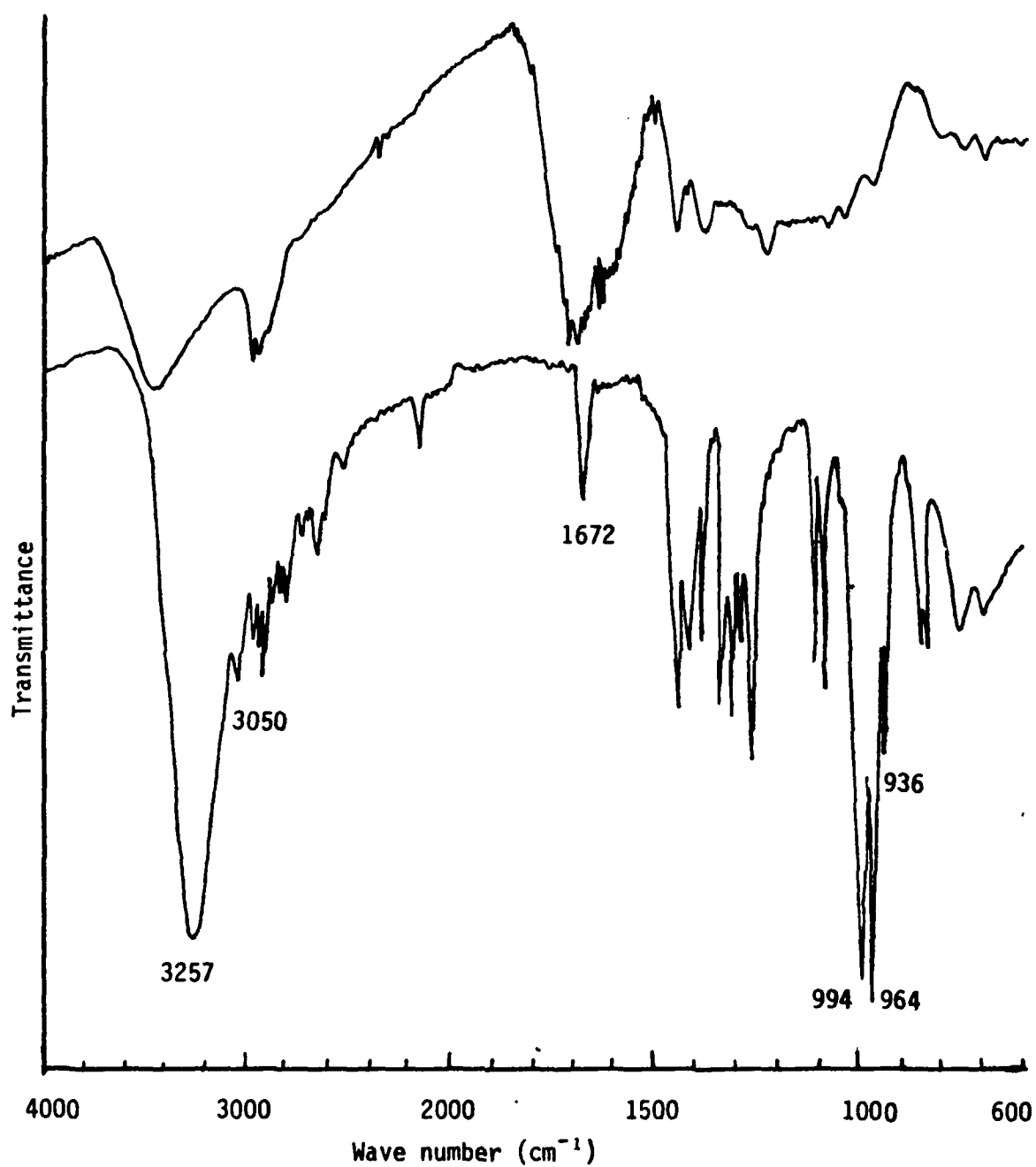


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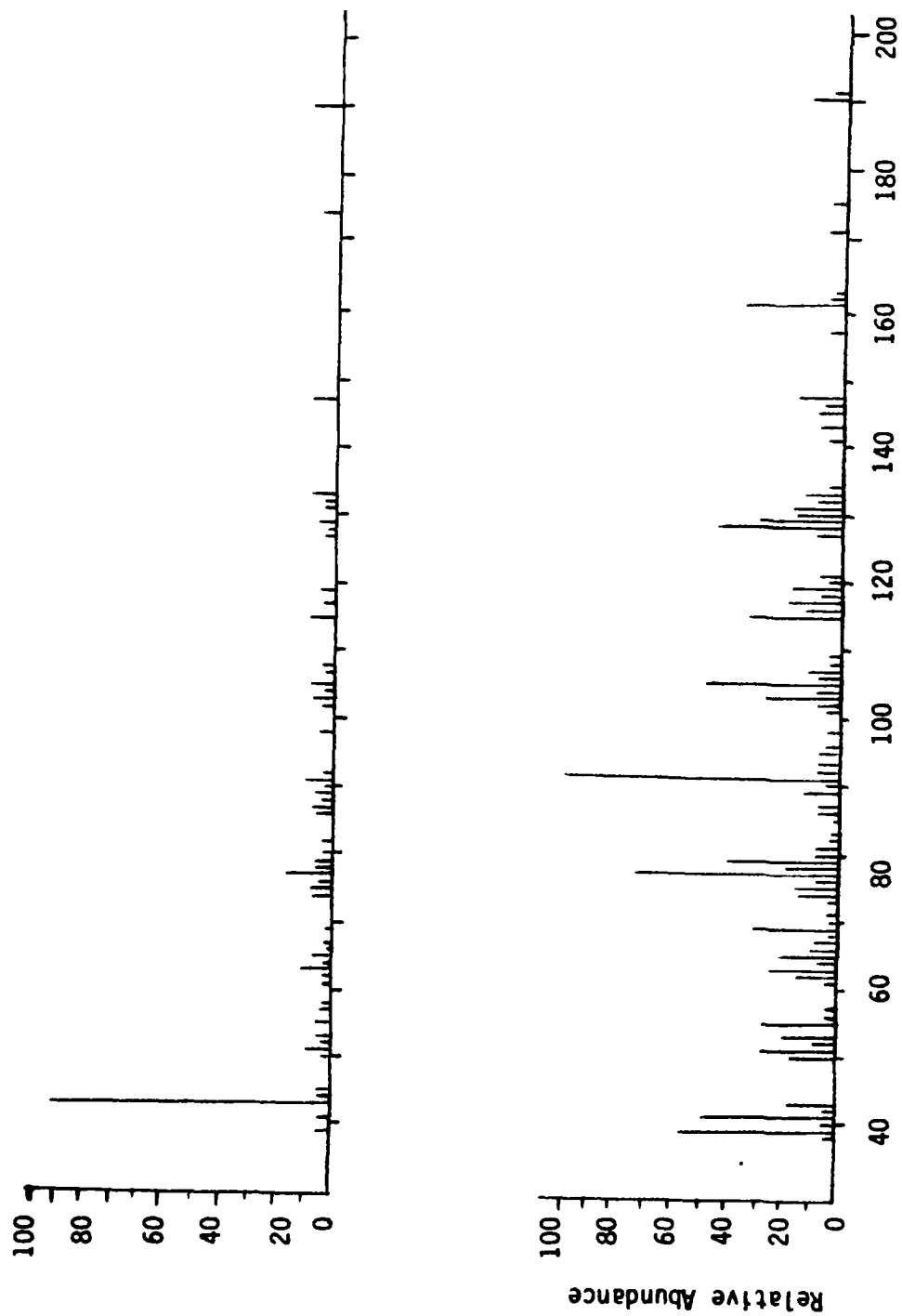
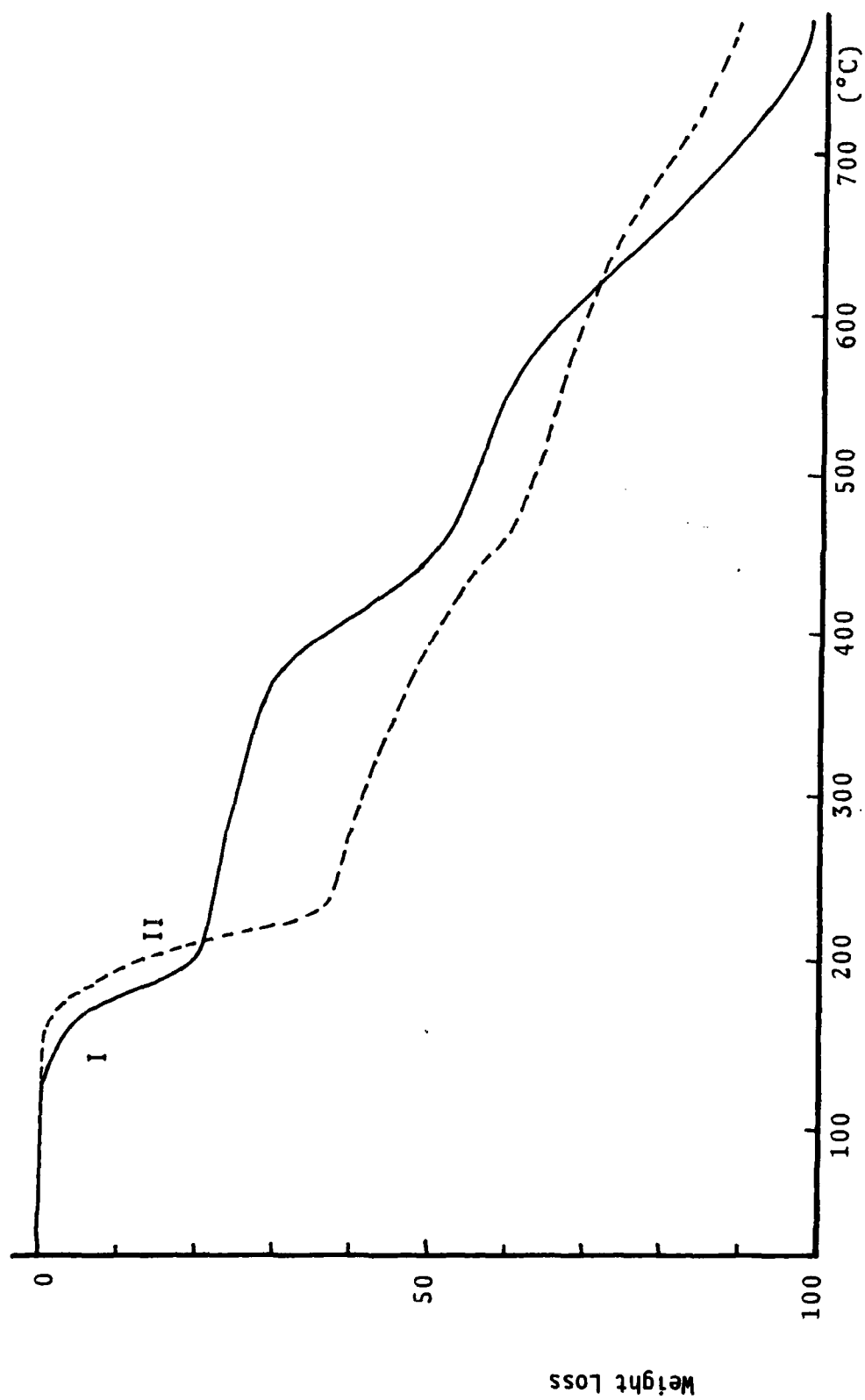
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FIGURE 6



Temperature

FIGURE 7

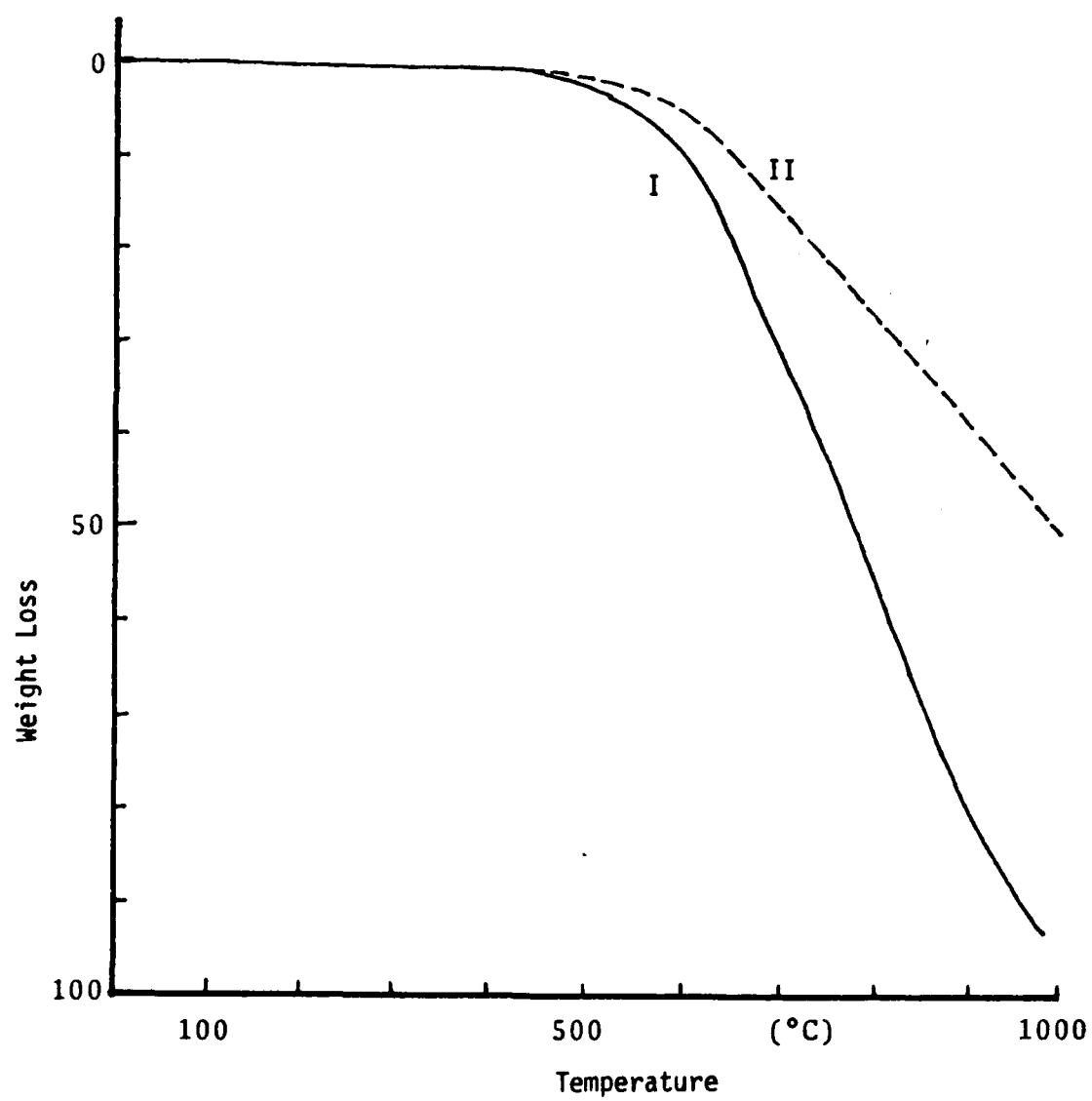


FIGURE 8

FIGURE LEGENDS

- Figure 1. DSC curve of (I) and (II). Heating rate 20⁰C/min in nitrogen.
- Figure 2. ¹H NMR spectra of dodeca-2,10-dien-5,7-diyn-4,9-diol (I) and dodeca-3,9-dien-5,7-diyn-2,11-diol (II), in CDCl₃-d₆ DMSO mixture.
- Figure 3. ¹³C NMR spectra of (I), decoupled (bottom) and coupled (top).
- Figure 4. ¹³C NMR spectra of (II), decoupled (bottom) and coupled (top).
- Figure 5. IR spectra of (I) (bottom) and its polymer (top) (KBr pellet).
- Figure 6. Mass-spectral decomposition of (I) and (II).
- Figure 7. TGA curve of (I) and (II) in nitrogen atmosphere at heating rate of 10⁰C/min.
- Figure 8. TGA curve of polymers, from (I) and (II) polymerized at 500⁰C for two hr, at heating rate of 10⁰C/min in nitrogen atmosphere.

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